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Structural and Conformational Properties of 1,2-Ethanedithiol as Studied by Microwave Spectroscopy and *Ab Initio* Calculations

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The microwave spectrum of 1,2-ethanedithiol has been re-investigated in the 10.0–39.0 GHz spectral region. Ten all-staggered rotameric forms are possible for this compound. The gas phase consists of a complex equilibrium mixture of several rotameric forms of the molecule. Four of these conformers, *gAg*, *gAg'*, *gGg* and *gGg'*, are presumed to predominate.

The assignments for one previously assigned conformer, *gGg*, have been extended. The assignments for two 'new' conformers, *gAg'* and *gGg'*, are reported for the first time.

The *gAg'* rotamer was found to be the most stable conformer that possesses a dipole moment different from zero. *gAg'* is 3.2(4) kJ mol^{-1} more stable than *gGg*, and 1.8(4) kJ mol^{-1} more stable than *gGg'*. In addition to these three rotamers, the *gAg* conformer having no dipole moment and hence not observable by microwave spectroscopy, is assumed to be a fourth stable, low-energy form of the molecule. The *gGg* rotamer is stabilised with one weak S–H ··· S intramolecular hydrogen bond, whereas *gGg'* is stabilised with two such bonds.

The *gAg'* conformer displays tunnelling in the ground vibrational state and in the first excited state of the C–C torsional vibration. The tunnelling is presumably caused by a concerted rotation by both thiol groups. The tunnelling frequency is 0.575(80) MHz in the ground vibrational state, and 2.48(5) MHz in the first excited state of the C–C torsion. Tunnelling is absent in the *gGg* and *gGg'* rotamers.

The microwave work has been assisted by *ab initio* computations at the HF/6-311++G** and MP2/6–311++G** (frozen core) levels of theory, as well as density theory calculations at the B3LYP/6-311++G** level. All ten all-staggered conformations were predicted to be 'stable' (minima on the energy hypersurface) in the HF/6-311++G** computations, nine were predicted to be stable in the B3LYP/6-311++G** calculations, while only five were predicted to be stable in the MP2/6-311++G** computations. The conformers predicted to be stable in the last-mentioned computations all have *gauche* arrangements for the H–S–C–C links of atoms. The *relative* energies of the different conformers were rather similar at all these three levels of theory in those cases where stable conformers were predicted. The agreement with experiment is found to be satisfactory. The best predictions of the rotational constants were found in the MP2/6-311++G** computations, which are therefore assumed to predict the most accurate geometries for the conformers.

The structural and conformational properties of 1,2-ethanedithiol have been investigated by vibrational spectroscopy,[1] gas-phase electron diffraction (ED),[2–4] microwave (MW) spectroscopy[5] and *ab initio* calculations.[6–10]

The title compound represents a complicated conformational problem because rotational isomerism is possible around the two C–S bonds as well as the C–C bond, with the result that as many as ten different all-staggered conformations may be 'stable' (i.e. minima on the potential energy surface). These ten forms are depicted in Figs. 1 and 2. In Fig. 1 the six rotamers having a S–C–C–S *gauche* arrangement are shown, while the four conformations having the said atoms in the *anti* position are drawn in Fig. 2.

In the ED studies[2–4] it was found that S–C–C–S *anti* and *gauche* conformers exist with an energy difference of

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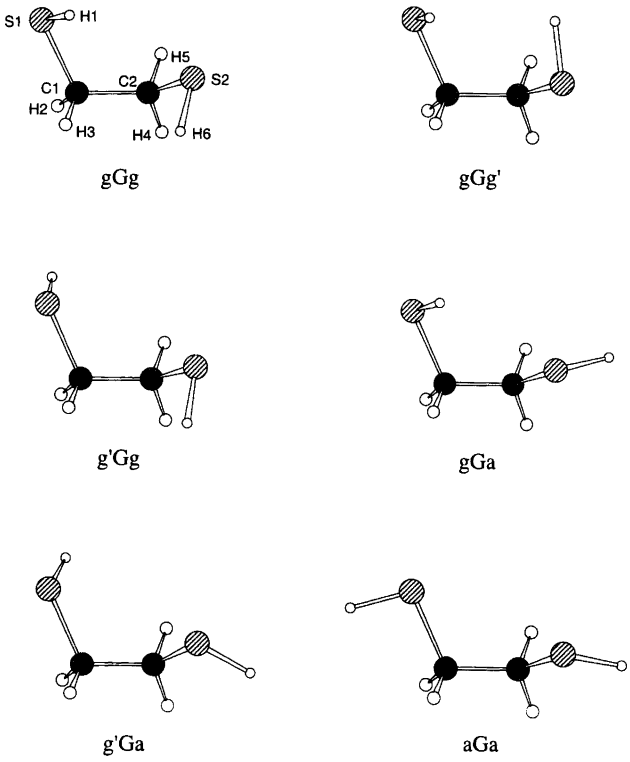

Fig. 1. The six all-staggered conformations of 1,2-ethanedithiol possessing a S–C–C–S *gauche* conformation. Atom numbering is shown on the *gGg* rotamer. *gGg* and *gGg'* were assigned in this work together with *gAg'* (Fig. 2). These three rotamers together with the non-polar *gAg* make up most of the gas phase. *gAg'* is the most stable conformer assigned in this work. It is 3.2(4) kJ mol^{-1} more stable than *gGg* and 1.8(4) kJ mol^{-1} more stable than *gGg'*.

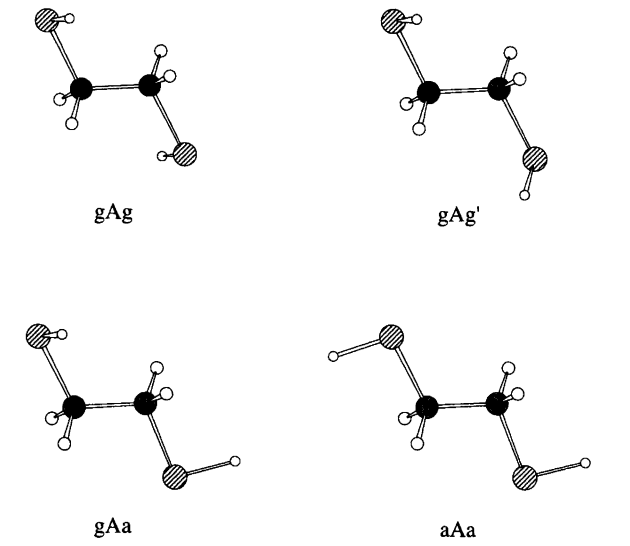

Fig. 2. The four all-staggered conformations of 1,2-ethanedithiol having a S–C–C–S *anti* conformation.

2–4 kJ mol^{-1} in favour of the *anti*. Exactly which *gauche* and *anti* rotamers that actually make up the gas phase and the relative energies of the individual rotamers could not be answered unambiguously[2–4] because the exact orientations of the S–H groups could not be determined with this method.

The ground vibrational state of one rotamer was assigned in the MW work and its dipole moment was determined.[5] The spectrum was observed to be dense, but no further assignments were given. The identified conformer was assumed to be *gGa*,[4,5] but this is not compatible with the *ab initio* computations reported below, which indicate that *gGg* rather than *gGa* had actually been assigned in Ref. 5.

In the most recent and elaborate *ab initio* work[10] complete optimisation was carried out at the HF/6-31++G** level for all 10 rotamers in Figs. 1 and 2. Single-point calculations at the MP2/6-31++G** level were also performed. In these computations[10] the *gAg* and *gAg'* conformers were predicted to have practically the same energy and to be the most stable forms of the molecule. The *gGg* and *gGg'* conformers were each computed to be about 2 kJ mol^{-1} less stable than the said two heavy-atom *anti* forms.

Microwave spectroscopy is ideal for investigating complicated conformational equilibria where several conformers are present because of its high selectivity and specificity. There was considerable indication both from the ED works,[2–4] the previous MW work[5] as well as from the most recent *ab initio* computations[10] that more conformers than just the one rotamer found in the MW work[5] would be present in such large concentrations that it might be possible to assign them. This was one motivation to re-investigate the MW spectrum of 1,2-ethanedithiol. Indeed, two additional rotamers, *gAg'* and *gGg'*, were assigned.

Another motivation to carry out the present work is our interest in intramolecular hydrogen (H) bonding and the possible role it might have in the title compound. The thiol group can act both as a donor and as an acceptor of H bonds in this case. Internal H bonds of the S–H ··· S type are possible in the *gGg*, *gGg'* and *gGa* conformations (Fig. 1). The *gGg'* rotamer has in fact two such H bonds. It has been pointed out[4,5,10,11] that the H bonds in 1,2-ethanedithiol must be rather weak, a view that is supported by this research.

High-level *ab initio* computations are often found to be useful in predicting rotational constants, dipole moments and energy differences for the various conformers that are sufficiently close to the experimental ones to be really helpful starting points in the spectral analysis. In addition, such computations may give important information about rotamers that for whatever reason have not been assigned by MW spectroscopy. Such calculations are therefore of interest also in their own right. Rather extensive computations have thus been carried out.

Experimental

The sample utilised in this work was purchased from Fluka. It was specified to be more than 98% pure by gas

Table 1. Structure, rotational constants and dipole moments of the six all-staggered heavy-atom *gauche* rotamers of $HSCH_2CH_2SH$ as calculated by *ab initio* at the HF/6-311++G** level[a] or at the MP2/6-311++G** level.[b]

Conformer:[c]	*gGg*	*gGg'*	*g'Gg*	*gGa*	*g'Ga*	*aGa*
Distance/pm						
S1–H1	133.6	133.5	133.6	133.0	133.2	133.1
C1–S1	181.3	181.5	181.4	182.2	182.2	183.0
C1–H2	109.5	109.5	109.4	108.3	108.3	108.2
C1–H3	109.4	109.3	109.4	108.3	108.3	108.2
C1–C2	152.6	152.6	152.7	152.6	152.4	152.4
C2–H4	109.4	109.5	109.4	108.3	108.3	108.2
C2–H5	109.3	109.3	109.4	108.1	108.3	108.2
C2–S2	181.7	181.5	181.4	182.9	183.0	183.0
S2–H6	133.7	133.5	133.6	133.0	133.1	133.1
Angle/°						
H1–S1–C1	95.2	96.0	95.4	98.5	97.7	96.8
S1–C1–H2	105.1	104.9	109.4	104.1	108.7	108.4
S1–C1–H3	110.3	109.6	105.4	109.6	104.9	109.5
S1–C1–C2	114.2	114.9	115.0	115.7	115.7	111.7
C1–C2–H4	109.8	108.8	109.2	108.9	108.3	108.2
C1–C2–H5	109.8	110.4	110.2	110.2	110.5	110.3
C2–C2–S2	114.3	114.9	115.0	110.9	112.2	111.7
C2–S2–H6	95.5	95.9	95.4	97.8	96.7	96.8
Dihedral angle[d]/°						
H1–S1–C1–H2	184.8	167.1	−58.1	176.3	−59.9	53.8
H1–S1–C1–H3	69.2	51.4	186.8	61.8	185.1	−64.6
H1–S1–C1–C2	−55.9	−73.4	65.2	−64.6	63.3	173.0
S1–C1–C2–H4	−169.2	−175.3	−171.6	−165.9	181.9	−173.2
S1–C1–C2–H5	−50.4	−57.0	−54.0	−46.2	−59.7	−54.4
S1–C1–C2–S2	67.8	67.5	65.0	74.9	62.6	67.6
C1–C2–S2–H6	64.6	−73.4	65.2	191.4	154.8	172.9
Rotational constants/MHz						
A	9433.6	9372.7	9401.1	9831.6	9324.3	9502.8
B	2216.3	2224.5	2173.4	2126.5	2217.8	2224.1
C	1927.7	1912.8	1913.2	1872.5	1917.9	1927.1
Principal-axis dipole moment component[e]/10^{-30} C m						
μ_a	2.67	0.00	0.00	3.97	2.30	0.00
μ_b	6.20	3.74	8.77	5.60	9.97	9.84
μ_c	3.24	0.00	0.00	1.67	3.47	0.00

[a]MP2/6-311++G** computations were made for the *gGg*, *gGg'* and *g'Gg* rotamers. [b]HF/6-311++G** calculations were made for *gGa*, *g'Ga* and the *aGa* conformations; see text. [c]See Fig. 1 for atom numbering. [d]Dihedral angle is zero for the eclipsed position. Clockwise rotation is defined to have a positive dihedral angle. [e]1 debye = 3.335 64 × 10^{-30} C m.

chromatography, and was used as received. No impurities were seen in the MW spectrum. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 12. The 10–39 GHz spectral region was investigated with the microwave absorption cell cooled to about −20 °C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 2–6 Pa when the spectra were recorded and stored electronically using the computer programs written by Waal.[13] The accuracy of the spectral measurements is presumed to be better than ±0.10 MHz. The maximum resolution is about 0.2 MHz at a pressure of ca. 2 Pa.

Results and discussion

Ab initio *calculations.* The Gaussian 94 program package[14] running on the IBM RS6000 cluster in Oslo was employed in all the *ab initio* calculations. The rather large 6-311++G** basis set provided with the program[14] was used throughout.

Three different computational schemes were employed. In the first calculations the geometries of all ten forms shown in Figs. 1 and 2 were fully optimised within the HF limit. All ten conformations were found to be minima (stable) on the potential energy surface in this case, as no imaginary vibrational frequencies[15] were computed for any of them.

Electron correlation was included next using the second order Møller–Plesset (MP2) perturbation theory[16] with frozen-core electrons.[14] The geometries were fully optimised in this case too using the HF/6-311++G** geometries obtained as described above as the starting points and the default criteria of convergence. Interestingly, only conformations having H–S–C–C in the *gauche* position were found as minima. In those cases where the H–S–C–C chain of atoms was in the *anti*

position in the beginning, the computations refined to a *gauche* position for this link of atoms. The failure of the MP2/6-311++G** computations to find stable H–S–C–C *anti* conformers is assumed to be an artefact of the computational procedure. Our reason for believing so is the fact that the closely related compound ethanethiol (CH_3CH_2SH) has an *anti* form[17,18] which is less stable than *gauche*[18] by 1.70(18) kJ mol^{-1}.

Finally, density functional theory calculations were carried out for two reasons. The first was to see whether this procedure produce rotational constants closer to the experimental ones than those computed at the HF/6-311++G** or MP2/6-311++G** levels. Secondly, it was interesting to see whether stable rotameric forms having the H–S–C–C chain in the *anti* position would be predicted. Calculations were thus made at the B3LYP/6-311++G** level[19] of theory allowing for full geometry optimisation for all ten rotamers of Figs. 1 and 2. In this case, all conformers but *gGa* were found to be stable. The failure to find *gGa* as a stable form, is again assumed to be an artefact of the computations.

In Tables 1 and 2 the geometries calculated for the ten rotamers are given. Atom numbering is given in Fig. 1. The MP2 structures are listed when available (for H–S–C–C *gauche* forms). In the other cases the HF structures are given (for H–S–C–C *anti* forms), because MP2 structures are not available. Our reason for selecting structures computed in two different ways is the fact that the rotational constants calculated by the MP2/6-311++G** procedure are definitely closer to the experimental ones than those calculated by the two other procedures (Table 3). It is seen in this table that the MP2 rotational constants agree with the observed ones better than to within 2%. The HF and B3LYP results deviate much more (up to 5%). The quality of HF and B3LYP computations seem to be about the same.

Small differences are normally found when r_0 rotational constants are compared with the r_e rotational constants. This is one reason why we believe that the MP2 structures are better representatives of the real structure than the HF or B3LYP structures are. Moreover, the structural parameters predicted in the MP2 computations are close to the corresponding r_s parameters determined in *anti*[18] and *gauche*[20] ethanethiol. r_s structures are generally close to r_e structures. It is therefore assumed that the MP2 structures (Table 1) represent the equilibrium structure better than the HF and B3LYP structures do. It is noted in Table 3 that the *B* and *C* rotational constants are computed to be too small in comparison with the experimental values in the HF as well as in the B3LYP calculations. This is typical when bond lengths that are too long are predicted. In particular, the C–S bond lengths seem to come out rather long in the HF and B3LYP computations in comparison with the r_s values in ethanethiol.[17,20]

Most bond lengths and bond angles vary little among the different conformers (Tables 1 and 2). However, one of the structural parameters, viz. the C–C–S angle, is calculated to change somewhat with the orientation of the thiol group. The C–C–S angle is 4–6° larger when the H–S–C–C atoms are *gauche* than when they are *anti*. A similar situation exists in ethanethiol.[17,20]

The energy differences found in the computations are shown in Table 4. The agreement between the three different computational schemes is seen to be good in those cases where stable rotamers are predicted. There is also good agreement with the HF/6-31++G** computations reported recently.[10] The *gAg* conformer, which has zero dipole moment, is computed to be the most stable form of the molecule. The *gAg'* rotamer is predicted to be almost equally stable in the HF, MP2 as well as in the B3LYP procedures. The *gGg* and *gGg'* are calculated to be the most stable heavy-atom *gauche* forms, 1–3 kJ mol^{-1} less stable than the two said *anti* conformers (Table 4). The energies of all rotamers fall within a relatively narrow range of about 15 kJ mol^{-1}. There is a trend that conformers having H–S–C–C *gauche* arrangements are preferred relative to similar ones having an *anti* orientation for this group. This has a parallel in the experimental findings for ethanethiol, where the *gauche* form is preferred.[18]

In the MW[5] and one ED[4] work it was assumed that the *gGa* conformer had been assigned. It is seen (Table 1) that the rotational constants of the *gGa* and *gGg* rotamers are predicted to be very similar. Comparison of the experimental rotational constants (Table 5) with the calculated ones (Table 1) is therefore inconclusive. However, the *ab initio* computations render additional evidence which may be used to discriminate between *gGg* and *gGa*. The experimental dipole moment and its components along the principal inertial axes[5] which were determined to be (in units of 10^{-30} C m) $\mu_a = 2.28(4)$, $\mu_b = 5.83(15)$, and $\mu_c = 2.58(7)$, respectively, are in better agreement with the values calculated for the *gGg* conformer than those computed for the *gGa* rotamer, as seen in Table 1. Moreover, the *gGg* rotamer is computed to be considerably more stable than *gGa* in HF/6-311++G** computations (3.2 and 7.8 kJ mol^{-1}, respectively, relative to *gAg*; Table 4). For these reasons it is assumed that conformer assignment[4,5] should be revised, and that the *gGg* rather than the *gGa* form was the conformer actually assigned in the MW work.[5]

The possible influence of intramolecular H bonding has been alluded to in earlier studies.[4,5,10] The non-bonded H1 ··· S2 distances are calculated to be 282.3, 306.7 and 304.7 pm from the structures in Table 1 for the *gGg*, *gGg'* and *gGa* isomers, respectively, which are the three forms of the molecule that are capable of having this interaction. These values are close to the sum of the van der Waals radii of hydrogen and sulfur (305 pm),[21] indicating that the H bonds are rather weak and represent borderline cases.

MW spectrum and extension of the assignments for the gGg *confomer*. It has already been noted[5] that the MW spectrum of 1,2-ethanedithiol is very dense with absorp-

Table 2. Structure, rotational constants and dipole moments of the four all-staggered heavy-atom *anti* rotamers of $HSCH_2CH_2SH$ as calculated by *ab initio* at the HF/6-311++G**[a] level or at the MP2/6-311++G** level.[b]

Conformer:[c]	*gAg*	*gAg'*	*gAa*	*aAa*
Distance/pm				
S1–H1	133.6	133.6	133.1	133.1
C1–S1	181.8	181.8	182.2	182.9
C1–H2	109.4	109.3	108.3	108.2
C1–H3	109.2	109.3	108.2	108.2
C1–C2	152.2	152.2	152.3	152.3
C2–H4	109.2	109.3	108.1	108.2
C2–H5	109.4	109.3	108.2	108.2
C2–S2	181.8	181.8	183.1	182.9
S2–H6	133.6	133.6	133.1	133.1
Angle/°				
H1–S1–C1	95.6	95.7	97.9	97.5
S1–C1–H2	105.2	105.8	105.0	109.1
S1–C1–H3	110.6	110.1	109.2	109.1
S1–C1–C2	112.7	112.7	113.1	108.9
C1–C2–H4	110.5	109.9	110.1	110.3
C1–C2–H5	110.1	110.7	110.4	110.3
C1–C2–S2	112.6	112.6	109.0	108.9
C2–S2–H6	95.6	95.7	97.5	97.5
Dihedral angle[d]/°				
H1–S1–C1–H2	178.1	179.6	170.3	59.6
H1–S1–C1–H3	62.2	63.7	55.1	−59.5
H1–S1–C1–C2	−61.9	−60.4	−69.2	180.0
S1–C1–C2–H4	−55.7	−57.1	−58.9	−60.3
S1–C1–C2–H5	62.9	61.5	61.3	60.2
S1–C1–C2–S2	180.0	185.2	181.0	180.0
C1–C2–S2–H6	61.8	−60.3	178.4	180.0
Rotational constants/MHz				
A	24926.1	24884.4	25411.3	25581.8
B	1495.5	1495.7	1493.2	1513.6
C	1455.8	1457.3	1447.0	1454.8
Prinicpal-axis dipole moment component[e]/10^{-30} C m				
μ_a	0.00	0.00	1.27	0.00
μ_b	0.00	0.00	4.44	0.00
μ_c	0.00	5.04	2.30	0.00

[a]MP2/6-311++G** computations were made for the *gAg* and *gAg'* conformations. [b]HF/6-311++G** were made for the *gAa* and *aAa* conformations. [c–e]Comments as for Table 1.

Table 3. Experimental[a] and theoretical (6-311++G** basis set) rotational constants/MHz.

	Exp.	HF	Diff. (%)	B3LYP	Diff. (%)	MP2	Diff. (%)
gAg'							
A	24750.4	25235.6	−2.0	24857.0	−0.4	24884.4	−2.0
B	1487.3	1473.2	1.0	1451.1	2.4	1495.7	−0.6
C	1451.1	1438.9	0.8	1417.6	2.3	1457.3	−0.4
gGg							
A	9292.5	9652.9	−3.9	9307.2	−0.2	9433.6	−1.5
B	2239.2	2127.5	5.0	2149.5	4.0	2216.3	1.0
C	1935.6	1866.9	3.6	1869.6	3.4	1927.7	0.4
gGg'							
A	9277.3	9505.0	−2.5	9320.8	0.4	9372.7	−1.0
B	2242.4	2153.3	4.0	2142.2	4.5	2224.5	0.8
C	1923.5	1866.4	3.0	1851.3	3.8	1912.8	0.6

[a]Taken from Tables 5, 7 and 9 below.

tions occurring every few MHz, an observation that was confirmed by us.

The high-J members of the ^bQ-transitions of the ground vibrational state of the *gGg* conformer are the strongest ones seen in the spectrum; their peak intensities being of the order of magnitude of 4×10^{-7} cm^{-1} at

Table 4. Energy differences *relative* to *gAg* obtained using the 6-311++G** basis set and different computational schemes.

	Relative energy/kJ mol^{-1}		
Calculation method:	HF[a]	B3LYP[b]	MP2[c]
gAg	0.0	0.0	0.0
gAg'	0.1	0.2	0.0
gGg'	2.8	2.3	2.2
gGg	3.2	2.2	0.9
gAa	3.9	5.4	—[d]
aAa	7.8	10.5	—[d]
gGa	7.8	—[d]	—[d]
g'Gg	10.2	10.1	10.1
g'Ga	11.6	11.2	—[d]
aGa	14.1	15.0	—[d]

Total energy of *gAg*: [a] −2 295 530.55, [b] −2 300 681.70 and [c] −2 297 053.70 kJ mol^{-1}. [d]Not found as a minimum on the energy hypersurface; see text.

−20 °C. The *gGg* conformer has the largest dipole moment of the three rotamers assigned here (Tables 1 and 2), with relatively large components along all three inertial axes. The statistical weight of *gGg* is 4, while the statistical weights of *gAg'* and *gGg'* are 2 in each case. The energy differences between *gGg* and the less polar but more stable *gAg'* and *gGg* conformers are not large (see below). The *gGg* form in fact contributes more of the strong transitions than either of the other two identified forms (*gAg'* and *gGg'*) in spite of the fact that it is the least stable assigned rotamer. A total of more than 1800 transitions of the rich spectrum of *gGg* were ultimately assigned.

55 transitions of the *a*-, *b*- and *c*- type varieties were previously[5] fitted for the ground vibrational state of the *gGg* rotamer. These assignments were readily extended to about 750 transitions, 670 of which were used to determine the spectroscopic constants (*A* reduction; I^r representation)[22] reported in Table 5.* The maximum value of *J* was 89. Four of the sextic centrifugal distortion constants had to be included in the least squares fit in order to get a fit with a root-mean-square deviation comparable to the experimental uncertainty of better than ±0.10 MHz.

Five excited vibrational states belonging to four different normal modes of this rotamer were then assigned for the first time; their spectroscopic constants are listed in Table 5. Relative intensity measurements performed largely as described in Ref. 23 yielded 134(15) cm^{-1} for what is assumed to be the torsional vibration around the C–C bond, 193(20) cm^{-1} for the lowest torsion around the C–S bond, ca. 235 cm^{-1} for the lowest bending vibration, and ca. 300 cm^{-1} for the second lowest torsion around

*The full spectra of the three conformers assigned in this work are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 5. Spectroscopic constants[a,b] of the ground and vibrationally excited states of the *gGg* rotamer of 1,2-ethanedithiol.

Vibrational state:	Ground vibrational state	1st ex. C–C tors. vibration	2nd ex. C–C tors. vibration	1st ex. lowest C–S torsional vibration	1st ex. lowest bending vibration	1st ex. second lowest C–S torsional vibration
No. of transitions:	670	442	112	199	149	34
R.m.s. dev. [c]/MHz:	0.072	0.071	0.103	0.075	0.089	0.072
A_v/MHz	9292.4756(17)	9383.4502(22)	9479.0284(65)	9264.0226(41)	9289.1874(41)	9346.517(15)
B_v/MHz	2239.20543(42)	2224.15194(53)	2208.9567(15)	2247.95702(94)	2234.6887(12)	2234.6953(80)
C_v/MHz	1935.55564(39)	1925.95354(48)	1916.3465(15)	1938.6065(12)	1932.4164(12)	1929.8277(79)
Δ_J/kHz	1.20890(46)	1.21878(45)	1.2490(16)	1.2377(22)	1.22207(95)	1.139(50)
Δ_{JK}/kHz	−8.9174(48)	−9.6145(52)	−10.238(24)	−9.136(18)	−9.101(12)	−10.293(57)
Δ_K/kHz	36.0587(46)	40.5076(56)	45.419(31)	35.894(11)	36.686(11)	43.5(15)
δ_J/kHz	0.27936(10)	0.28279(11)	0.28609(68)	0.29148(58)	0.28217(38)	0.3053(11)
δ_K/kHz	2.762(13)	2.914(13)	3.217(56)	2.874(39)	2.875(33)	3.344(90)
Φ_J/Hz	0.000313(24)	0.000261(28)	0.01213(84)	0.00063(20)	0.00543(21)	—[f]
Φ_{JK}/Hz	0.05243(52)	0.04937(46)	0.254(19)	0.0608(39)	0.0374(42)	—[f]
Φ_{KJ}/Hz	−0.3356(35)	−0.3880(58)	—[f]	−0.336[g]	—[f]	—[f]
Φ_K[e]/Hz	0.998(13)	1.226(23)	—[f]	0.998[g]	—[f]	—[f]
Max. value of *J*	89	90	59	75	56	29

[a]*A*-reduction, I^r-representation.[22] [b]Uncertainties represent one standard deviation. [c]Root-mean-square deviation. [e]Further sextic centrifugal distortion constants kept constant at zero in the least-squares fit. [f]Kept constant at zero in the least-squares fit. [g]Kept constant at this value in the least-squares fit.

the C–S bond. The corresponding values found in the B3LYP/3-311++G** computations (not reported in Table 1) were 126, 214, 239 and 302 cm^{-1}, respectively, in good agreement with our relative intensity measurements.

It is interesting to compare the MW spectra of the *gGg* conformer with those of its oxygen congener, 1,2-ethanediol, $HOCH_2CH_2OH$. Two conformers corresponding to *gGg* and *gGa* have been assigned for 1,2-ethanediol.[24–27] The spectra of both these rotamers display large (several GHz) splittings presumably caused by a concerted tunnelling of the two alcohol groups. Such a feature is completely absent in the spectrum of the *gGg* conformer of the title compound within the resolution of our experiment (0.2 MHz). The barrier to tunnelling is perhaps much larger in the case of the *gGg* conformer of 1,2-ethanedithiol than in the corresponding rotamer of 1,2-ethanediol and this may perhaps explain the absence of tunnelling in the present case.

MW spectrum and assignment of the ground vibrational state of gAg′. The *ab initio* calculations above indicate that *gAg* is the most stable form of 1,2-ethanedithiol (Table 3). However, this rotamer has *zero* dipole moment (Table 2) for symmetry reasons, and therefore cannot be observed by MW spectroscopy. The rotamer with the second lowest energy is predicted to be *gAg′*. This conformer is computed to be slightly less stable than *gAg* (Table 3), and it was therefore decided to search for this rotamer next.

The rotational constants in Table 2 indicate that *gAg′* is an almost prolate symmetrical top with the asymmetry parameter $\kappa \approx -0.99$. The dipole moment is calculated (Table 2) to lie along the *c*-inertial axis for symmetry reasons. The MW spectrum was thus predicted to possess a series of *c*-type $K_{-1} = 1 \leftarrow 0$ *Q*-branch transitions in the 20–10 GHz range. The intensities of these transitions would increase with increasing value of *J*. The survey spectra taken in this region revealed a series of comparatively strong transitions split by about 1.2 MHz into two components of equal intensity. These lines with *J* between 15 and 25 were used to derive the first assignments. ^cQ-transitions of this *Q*-branch series up to $J = 44$ of this series were then assigned. Searches were next made for the $K_{-1} = 2 \leftarrow 1$ ^cQ-branch series which was soon found. Maximum *J* for this series was 94. These transitions were also split by approximately the same amount as the previous $K_{-1} = 1 \leftarrow 0$ series. The assignments of intermediate-*J* *c*-type *R*-branch transitions were now made after some searching. These transitions were also split. Representative examples are given in Table 6.

Our explanation for the doublet splittings is that they arise from a concerted large-amplitude motion involving *both* thiol groups. A rotation of approximately 120° around both the C–S bonds (Fig. 2) produces a conformation that is spectroscopically identical to one depicted for *gAg′* in this figure. A double-minimum potential is associated with this motion. The exact path of this motion cannot be inferred from the MW spectrum.

Table 6. Selected transitions from the MW spectrum of the ground vibrational state of *gAg′* of 1,2-ethanedithiol.

Transition $J'_{K'-1,K'+1} \leftarrow J''_{K''-1,K''+1}$		Observed frequency[a] MHz	Obs.-calc. freq. MHz
$8_{1,8} \leftarrow 8_{0,8}$	(−)←(+)	22637.52	0.02
	(+)←(−)	22635.88	−0.06
$13_{0,13} \leftarrow 12_{1,11}$	(−)←(+)	13457.38	0.09
	(+)←(−)	13455.66	−0.07
$15_{1,15} \leftarrow 15_{0,15}$	(−)←(+)	21186.72	−0.03
	(+)←(−)	21185.20	−0.02
$16_{0,16} \leftarrow 15_{1,14}$	(−)←(+)	21454.11	−0.05
	(+)←(−)	21452.62	0.02
$17_{0,17} \leftarrow 16_{1,15}$	(−)←(+)	24075.33	0.00
	(+)←(−)	24073.84	0.06
$20_{0,20} \leftarrow 19_{1,18}$	(−)←(+)	31798.21	0.03
	(+)←(−)	31796.72	0.09
$19_{1,19} \leftarrow 19_{0,19}$	(−)←(+)	20035.09	0.01
	(+)←(−)	20033.60	0.02
$22_{0,22} \leftarrow 21_{1,20}$	(−)←(+)	36823.82	0.09
	(+)←(−)	36822.15	−0.03
$23_{1,23} \leftarrow 23_{0,23}$	(−)←(+)	18691.05	−0.02
	(+)←(−)	18689.48	−0.11
$28_{1,28} \leftarrow 28_{0,28}$	(−)←(+)	16805.44	−0.04
	(+)←(−)	16803.99	−0.03
$32_{1,32} \leftarrow 32_{0,32}$	(−)←(+)	15191.19	−0.01
	(+)←(−)	15189.62	−0.12
$36_{1,36} \leftarrow 36_{0,36}$	(−)←(+)	13538.03	0.01
	(+)←(−)	13536.53	−0.04
$61_{2,60} \leftarrow 61_{1,60}$	(−)←(+)	38990.27	0.01
	(+)←(−)	38988.85	0.06
$66_{1,65} \leftarrow 66_{0,65}$	(−)←(+)	34686.81	−0.05
	(+)←(−)	34685.49	0.08
$70_{2,69} \leftarrow 70_{1,69}$	(−)←(+)	31263.25	−0.03
	(+)←(−)	31261.79	−0.08
$77_{2,76} \leftarrow 77_{1,76}$	(−)←(+)	25469.81	−0.03
	(+)←(−)	25468.33	−0.05
$83_{2,82} \leftarrow 83_{1,82}$	(−)←(+)	20864.20	0.06
	(+)←(−)	20862.72	0.05
$86_{2,85} \leftarrow 86_{1,85}$	(−)←(+)	18730.54	0.06
	(+)←(−)	18729.05	0.03
$91_{2,90} \leftarrow 91_{1,90}$	(−)←(+)	15466.77	−0.06
	(+)←(−)	15465.34	−0.04

[a] ±0.10 MHz.

The spatial direction of the *c*-dipole moment component is inverted in this transformation. The ground state is a symmetrical or (+) state, while the first excited state of this double minimum potential is an antisymmetrical or (−) state. The separation between these states, Δ, is about half the splitting (about 0.5 MHz) observed for the *c*-type transitions. The selection rules are those of a rigid rotor plus (−)←(+), or (+)←(−) for the *c*-type transitions. The *c*-type lines should thus be split into two components with frequencies roughly equal to the rigid-rotor frequency plus or minus ca. 0.5 MHz.

In order to derive the spectroscopic constants of this tunnelling motion the computer program ASMIXX written by Nielsen[28] was utilised. This program employs an effective two-level rotation–vibration Hamiltonian, including quartic and sextic centrifugal distortion con-

stants and coupling terms of the μ- or *L*-type.[28,29] The reduced Hamiltonian has the following definition:[28]

$$H_{red} = |0\rangle\{H_r^{(0)} + H_d^{(0)}\}\langle 0| + |1\rangle\{H_r^{(1)} + H_d^{(1)} + W_{01}\}\langle 1| + |0\rangle H_c\langle 1| + |1\rangle H_c < 0|$$

where the label 0 corresponds to the (+)-state and the label 1 to the (−)-state.

Using I^r representation[22] one has:

$$H_r^{(v)} = B^{(v)}J_b^2 + C^{(v)}J_c^2 + A^{(v)}J_a^2$$

where v refers to the (+) or (−) state, respectively.

$$H_d^{(v)} = \{\text{Watson quartic and sextic centrifugal distortion}\}^{(v)}$$

$$W_{01} = \langle 1|H_{vib}{}^0|1\rangle - \langle 0|H_{vib}{}^0|0\rangle$$

If the symmetry of the tunnelling mode is of *A* symmetry of the C_2 group, the coupling terms are given by

$$H_c = \mu_{ab}(J_bJ_a + J_aJ_b) \quad \text{or} \quad L_cJ_c$$

A total of 142 transitions were assigned for the ground vibrational state of the *gAg'* rotamer and used to derive the spectroscopic constants shown in Table 7. In the least-squares procedure used to derive the parameters of this table, the rotational constants and three of the quartic centrifugal distortion constants of both the (+)- and the (−)-states were fitted simultanously together with the separation between the (+)- and the (−)-state, $\Delta = W_{01}$. The use of only three quartic centrifugal distortion constants is warranted because *gAg'* is almost a symmetrical rotor. Inclusion of sextic centrifugal distortion constants yielded no improvement. Attempts were made to include μ- or *L*-type coupling terms in the least squares fit, but no significant values could be determined for these Coriolis coupling terms. Our model yields a good fit to the observed frequencies, as shown in Table 6, as the root-mean-square deviation is 0.058 MHz, comparable to the experimental uncertainty.

Inspection of Table 7 reveals that there is a small, but significant difference between the *A* rotational constants of the (+)- and (−)-states of 0.43 MHz, and insignificant differences between the *B* and the *C* rotational constants of the two states. A difference is seen for the Δ_{JK} Watson[22] centrifugal distortion constant of the two states whereas the Δ_J and δ_J centrifugal distortion constants are quite similar for the (+)- and (−)-state.

Table 7. Spectroscopic constants[a,b] of the (+)- and (−)-states of *gAg'* of 1,2-ethanedithiol in the ground vibrational state.

No. of transitions:	142	
R.m.s. dev.[c]/MHz:	0.058	
	(+)-state	(−)-state
A_v/MHz	24 750.393(92)	24 750.828(93)
B_v/MHz	1487.2781(15)	1487.2782(15)
C_v/MHz	1451.0747(15)	1451.0746(15)
Δ_J/kHz	0.1509(18)	0.1508(18)
Δ_{JK}/kHz	−1.194(44)	−0.973(43)
Δ_K/kHz	[d]	[d]
δ_J/kHz	0.005 892 3(62)	0.005 877 6(66)
δ_K/kHz	[d]	[d]
Δ^e/MHz	0.575(80)	

[a]As defined by Nielsen.[28] [b]Uncertainties represent one standard deviation. [c]Root-mean-square deviation. [d]Pre-set at zero in least-squares fit. [e]$\Delta = W_{01}$ (energy separation between the + and − states).

The *gAg'* rotamer belongs to the C_2 point group. If significant values for the μ- or *L*-type coupling terms had been available, it would have been possible to say what symmetry the tunnelling coordinate would have. The small difference in the *A* rotational constants may indicate that coupling occurs via the L_aJ_a term which belong to the *B* symmetry species of the C_2 point group.

The *gAg'* conformer of 1,2-ethanedithiol is the first example of a molecule possessing *two* thiol groups exhibiting tunnelling. For molecules having one such group, tunnelling is well known, e.g. in the case of *gauche* ethanethiol where a tunnelling frequency, Δ, of 1754.09 MHz has been reported.[18]

Attempts to determine the dipole moment by Stark effect measurements failed because the low-*J* transitions were so weak that quantitative measurements could not be made despite the fact that *gAg'* is the most stable polar rotamer. The reasons for this weakness is a moderately large dipole moment (Table 2), a splitting of each transition into two components, a large Boltzmann partition function, and the presence of several rotamer producing a mole fraction of rather moderate size for this rotamer.

The ground-state spectrum was accompanied by satellite spectra that could be ascribed to vibrationally excited states of *gAg'*. The first excited state of what is presumed to be the torsional vibration around the C–C bond, were assigned. The transitions of this excited state were also split in a similar way as seen for the ground state. However, the splittings were somewhat larger, about 5 MHz. A total of 58 transitions with a maximum value of $J = 44$ were assigned. The centrifugal distortion constants and the tunnelling frequency, Δ, did not refine properly in this case. Δ was fixed at 2.48 MHz and the centrifugal distortion constants at the values shown in Table 8 in the final refinements. The standard deviation of Δ is estimated to be ±0.05 MHz.

Eleven ^cQ-branch transitions of another vibrationally excited state were observed. No obvious splittings were observed here, either because they are very small, or alternatively very large. In this case $A - C =$ 23 276.658(60) MHz and $\kappa = -0.996\,883$ were determined. This may be the first excited state of the C–S torsional mode.

Relative intensity measurements yielded a frequency of 119(20) cm^{-1} for the first excited state of the C–C torsional vibration, compared to 111 cm^{-1} found in the B3LYP/6-311++G** computations above (not given in Table 2).

Assignment of gGg'. This rotamer is computed to be 2–3 kJ mol^{-1} (Table 4) less stable than *gAg*. It is pre-

Table 8. Spectroscopic constants[a,b] of the (+)-and (−)-states of the first excited state of the C–C torsional mode of *gAg′* of 1,2-ethanedithiol.

No. of transitions:	58	
R.m.s. dev.[c]/MHz:	0.133	
	(+)-state	(−)-state
A_v/MHz	24 027.103(68)	24 026.929(58)
B_v/MHz	1487.9934(22)	1487.9950(22)
C_v/MHz	1453.2462(20)	1453.2458(20)
Δ_J/kHz	0.151[f]	0.151[f]
Δ_{JK}/kHz	−1.08[f]	−1.08[f]
Δ_K/kHz	[d]	[d]
δ_J/kHz	0.005 90[f]	0.005 90[f]
δ_K/kHz	[d]	[d]
Δ^e/MHz	2.48[f,g]	

[a–e]Comments as for Table 7. [f]Pre-set at this value. [g]One standard deviation estimated to be ±0.05 MHz.

dicted to have only a *b*-axis dipole moment component that is different from zero for symmetry reasons (Fig. 1). Searches for the ^bQ-lines predicted to be the strongest ones for this rotamer were soon successful. The ^bR-branch transitions were found next after some searching. The assignments were then extended to include ultimately about 300 transitions, with a maximum value of $J = 73$ 276 of these were used to determine the spectroscopic constants listed in Table 9.

The dipole moment could not be determined for this rotamer because of insufficient intensities of low-*J* lines. The reason for this is similar to that discussed above for the *gAg′* rotamer.

Searches for *a*- and *c*-type transitions were futile although their hypothetical frequencies could be very accurately predicted from the spectroscopic constants in Table 9. This is one indication that only μ_b is different from zero, which is a prerequisite for this conformer.

Moreover, the way in which the lines of this rotamer are Stark modulated as well as their intensities indicate that μ_b is about 3.5×10^{-30} C m. Confusion of *gGg′* with any other heavy-atom *gauche* rotamer is thus definitely ruled out, because the dipole moments are so different (Table 1).

Two vibrationally excited states were assigned for *gGg′*, as shown in Table 9. The frequency of the C–C torsion was determined to be 123(20) cm^{-1}, and the frequency for the lowest C–S torsion to be ca. 200 cm^{-1}. The B3LYP/6-311++G** values were 114 and 172 cm^{-1}, respectively.

MW searches for further conformations. The above assignments include about 2500 transitions in the 10–39 GHz region. All the strongest transitions seen in the MW spectrum, the majority of the lines of intermediate intensity, as well as many weak lines have been assigned. Numerous unsuccessful attempts were made to assign unidentified transitions of intermediate intensities to each of the polar conformers that had not been detected. These unsuccessful searches concentrated mostly on the *gAa* and *gGa* rotamers, which are the two polar forms that are predicted to come closest in energy to the assigned ones (3.9 and 7.8 kJ mol^{-1} relative to *gAg* according to the HF computations; Table 4). The starting points in these searches were the rotational constants and dipole moment components given in Tables 1 and 2.

The fact that each of these conformations is predicted to possess sizeable dipole moments, as well as the observation that no strong unassigned lines remain, is evidence that additional polar unassigned forms must have relatively high energies compared to the energy of *gAg′* (and in all likelihood the unpolar *gAg* conformer). Our conservative estimate is that *gAg′* is at least 4 kJ mol^{-1} more stable than any hypothetical, fourth *polar* conformer. This estimate agrees well with the theoretical predictions in Table 4.

The most likely explanation for the comparatively weak and numerous unassigned transitions is that they

Table 9. Spectroscopic constants[a,b] of the ground and vibrationally excited states of the *gGg′* rotamer of 1,2-ethanedithiol.

Vibrational state:	Ground vibrational state	1st ex. C–C tors. vibration	2nd ex. C–C tors. vibration
No. of transitions:	276	51	41
R.m.s. dev.[c]/MHz:	0.075	0.078	0.103
A_v/MHz	9277.3431(39)	9359.691(12)	9265.164(41)
B_v/MHz	2242.376 13(93)	2230.1864(42)	2243.5223(63)
C_v/MHz	1923.4608(10)	1915.5806(40)	1926.2921(62)
Δ_J/kHz	1.2967(28)	1.288(15)	1.342(41)
Δ_{JK}/kHz	−9.895(28)	−10.608(45)	−9.363(54)
Δ_K/kHz	40.132(19)	45.0(13)	37.0(13)
δ_J/kHz	0.305 17(49)	0.305 57(87)	0.2957(10)
δ_K/kHz	3.114(37)	3.267(64)	2.919(81)
Φ_J/Hz	0.0082(22)	—[f]	—[f]
Φ_{JK}/Hz	0.211(46)	—[f]	—[f]
Φ_{KJ}/Hz	−0.355(18)	—[f]	—[f]
Φ_K^e/Hz	1.402(92)	—[f]	—[f]
Max. value of *J*	73	29	29

[a–f]Comments as for Table 5.

mainly belong to unassigned vibrationally excited states of *gAg'*, *gGg*, and/or *gGg'*. Small fractions of further rotamers cannot, however, be completely ruled out.

Energy differences. The energy differences between the three conformers assigned in this investigation were made by relative intensity measurements observing the precautions of Ref. 23. The MP2/6-311++G** dipole moment components in Tables 1 and 2 were used with any correction for vibrational dependence, because experimental dipole moments are not available in all cases. The HF or B3LYP dipole moments (not reported herein) deviate less than about 10% from the MP2 values. Use of any of these dipole moments instead of the MP dipole moments would have yielded results that would have deviated insignificantly from those reported here. The squares of the *ratios* of the dipole moments are used to derive the energy differences. It is therefore expected that systematic errors in the computed dipole moments would tend to largely to cancel. Large uncertainties in the energy differences resulting from the use of computed dipole moments are thus not expected.

The statistical weight of the *gGg* conformer was assumed to be twice that of each of *gAg'* and *gGg'* (see above). However, the statistical weights of the *individual* rotational levels are different in the *gGg'* and *gAg'* because they both contain a two-fold axis of symmetry. A 180° rotation interchanges three pairs of fermions (H atom pairs) and two pair of bosons (the carbon pair and the sulfur pair). The nuclear statistical weights are hence 28 for symmetrical rotational energy levels and 36 for antisymmetrical levels.[30] These statistics were taken into account in the derivation of the energy differences.

It was found that the *gAg'* rotamer is the most stable one of the *assigned* conformers. Whether it is more stable than the unpolar *gAg* conformer, which is predicted in all the theoretical computations to be the most stable form of the molecule, is impossible to say. *gAg'* is found to be 3.2(4) kJ mol^{-1} more stable than *gGg*, and 1.8(4) kJ mol^{-1} more stable than *gGg'*. The uncertainties given here are estimated to be one standard deviation. They have been estimated by taking the experimental uncertainties as well as the uncertainties of the calculated dipole moments into account and are considered to be liberal.

It is interesting to note that *gGg*, which has one S–H ··· S hydrogen bond, is slightly less stable (by 1.4 kJ mol^{-1}) than *gGg'*, which has two such bonds. The present findings are compared with the theoretical predictions in Table 10. The agreement is satisfactory.

Structure. The MP2/6-311++G** structures appear to be more accurate than the HF or B3LYP structures (see discussion in the *ab initio* section above). No experimental data are at hand that could really improve the MP2 structures shown in Tables 1 and 2, and they are therefore adopted as *plausible* structures for the *gAg'*, *gGg* and *gGg'* conformers. It is expected that any full experimental structures that might be determined in the future for these three rotamers will be close to the ones shown in these two tables.

Table 10. Experimental and theoretical (6–311++G** basis set)[a] energy differences relative to the energy of *gAg'*.

	Energy difference/kJ mol^{-1}			
	Exp.[b]	HF	MP2	B3LYP
$E_{gGg} - E_{gAg'}$	1.8(3)	3.1	0.9	2.0
$E_{gGg'} - E_{gAg'}$	3.2(4)	2.7	2.2	2.1

[a]Taken from Table 3. [b]Uncertainties represent one standard deviation.

Conclusions

This study has demonstrated that gaseous 1,2-ethanedithiol consists of a complex equilibrium mixture where four rotameric forms, *gAg*, *gAg'*, *gGg* and *gGg'* (Figs. 1 and 2), make up most of the gas phase. The three last-mentioned ones have been observed by MW spectroscopy, while the *gAg* rotamer is unpolar and cannot be determined by this method. However, three different high-level quantum chemical computations predict that *gAg* is the most stable form of the molecule. The two heavy-atom *anti* forms *gAg* and *gAg'* are 2–3 kJ mol^{-1} more stable than the two *gauche* conformers, *gGg* and *gGg'*. Weak intramolecular H bonds are stabilising the *gGg* and *gGg'* rotamers.

The conformational properties of $HSCH_2CH_2SH$ are strikingly different from those of its diol analogue, $HOCH_2CH_2OH$. In the latter compound conformers corresponding to *gGa* and *gGg* are the most stable ones.[24–27] Extensive tunnelling of the hydroxyl groups take place in the 1,2-ethanediol.[24–27] This tunnelling has no counterpart in the 1,2-etanedithiol.

$HSCH_2CH_2SH$ resembles its isoelectronic congener $H_2PCH_2CH_2PH_2$[31] in that heavy-atom *anti* forms are the most stable forms of the two molecules. A difference exists, however. While intramolecular H bonding seems to stabilise the title compound, this effect is of practically no importance for $H_2PCH_2CH_2PH_2$.[31]

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